PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-226334
(43)Date of publication of application : 22.08.1995

(51)Int.Cl. H01G 4/33
H01G 4/40

(21)Application number : 06-015180
(22)Date of filing : 09.02.1994

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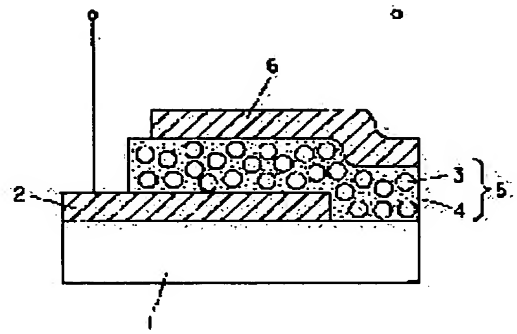
(54) THIN FILM CAPACITOR AND ITS MANUFACTURE

(57)Abstract:
PURPOSE: To provide a method of manufacturing a thin film capacitor of excellent insulating properties at a specific temperature or lower and a CR circuit device provided with the thin film capacitor and high in accuracy and reliability.
CONSTITUTION: A thin film capacitor is composed of a PC (polycarbonate) printed board 1, a lower aluminum electrode 2, a dielectric film 5 composed of composite perovskite oxide powder 3 and hardening resin 4, and an upper aluminum electrode. Composite perovskite oxide powder 3 of permittivity a few thousands or above is dispersed into volatile solvent which contains hardening resin 4, the disperse system is applied onto the PC printed board 1 through a spin coating method, the printed board 1 is heated at a temperature of 80° C and dried out by removing the volatile solvent by heating, and the hardening resin contained in the solvent is hardened by irradiation with ultraviolet rays to form a dielectric film 5 at a temperature of 150° C or below.



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[Date of request for examination]
[Date of sending the examiner's decision of rejection]
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
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[Date of registration]
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[Date of requesting appeal against examiner's decision of rejection]
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CLAIMS

[Claim(s)]
[Claim 1] The thin film capacitor which is a thin film capacitor which prepared the dielectric film between the lower electrode and the up electrode, and carries out the description of having used the mixture of compound perovskite oxide and hardenability resin as a dielectric film.
[Claim 2] The thin film capacitor according to claim 1 which uses a compound perovskite oxide as powder and is characterized by the particle size of the powder being 0.4 micrometers - 1.4 micrometers.
[Claim 3] The thin film capacitor according to claim 1 which uses a compound perovskite oxide as powder and is characterized by the addition of the hardenability resin to the powder being 0.5vol(s)% - 7vol%.
[Claim 4] The thin film capacitor according to claim 1 characterized by using ultraviolet-rays hardening resin as hardenability resin.
[Claim 5] For the principal component of a compound perovskite oxide, an empirical formula is ABO3. Thin film capacitor according to claim 1 characterized by being expressed, containing at least one sort of Pb, Sr, Ba, and La as A, and containing at least one sort of Ti, Zr, Ta, Mg, and Nb as B.
[Claim 6] The manufacture approach of the thin film capacitor characterized by having formed the lower electrode on the substrate, having prepared the mixture of compound perovskite oxide powder and hardenability resin on said lower electrode, having stiffened said hardening resin at the temperature of 150 degrees C or less after that, having formed the dielectric film, and forming an up electrode on said dielectric film.
[Claim 7] The manufacture approach of the thin film capacitor according to claim 6 which uses hardenability resin as ultraviolet-rays hardening resin, and is characterized by irradiating ultraviolet rays and forming a dielectric film.
[Claim 8] CR circuit element which is a CR circuit element which combined resistance and a capacitor electrically, and is characterized by using a thin film capacitor according to claim 1 as a capacitor.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the thin film capacitor widely used for a public welfare device etc., and its manufacture approach.
[0002]
[Description of the Prior Art] When forming a thin film capacitor on the printed circuit board made of resin, the cure against heat at the time of the dielectric membrane formation process of having taken into consideration the heat-resistant temperature of a resin substrate is an important technical technical problem. As a conventional technique, it is SiO2 by electron cyclotron resonance vapor growth (ECR-CVD method). The approach of forming the thin film capacitor using the film on a glass epoxy group plate with a heat-resistant temperature of 200 degrees C is announced by the 126th page from the 123rd page (1993) of the 5th microelectronics symposium collected works.
[0003]
[Problem(s) to be Solved by the Invention] SiO2 formed with the ECR-CVD method The capacity consistencies of a dielectric film capacitor are 13.1 nF/cm2. Although the property of practical use level is acquired, considering cost performance, the capacity consistency of 5 times or more is required. In order to attain one 5 times the capacity consistency of this, dielectric thickness had to be set to one fifth of 60nm, and there was a problem on which insulation deteriorates.
[0004] This invention solves said conventional technical problem, and is 70 nF/cm2. While aiming at offering the thin film capacitor which has the above capacity consistency and was excellent in insulation, and its manufacture approach, it aims at offering CR circuit element of high degree of accuracy and high-reliability using it.
[0005]
[Means for Solving the Problem] In order to attain this object, particle size fabricated the compound perovskite oxide powder which is 0.4 micrometers - 1.4 micrometers using 0.5vol(s)% - 7vol% hardenability resin as a dielectric film.
[0006]
[Function] The dielectric film which uses as a principal component the compound perovskite oxide with which a dielectric constant has thousands or more and is used for a ceramic condenser by the aforementioned means can be formed at the low temperature of 150 degrees C. Hardenability resin is used in order to bind compound perovskite oxide powder, but since the effective dielectric constant of a dielectric film will fall if the volume fraction of hardenability resin increases, 0.5vol% - 7vol% is the optimal. The particle size of compound perovskite oxide acts on a binding property and electric insulation. In 0.4 micrometers or less, surface area becomes large, and it becomes impossible for particle size to fully bind by 7vol% hardenability resin. Moreover, the opening between the grains with which particle size is set to 1.4 micrometers or more becomes large, and electric insulation deteriorates. Therefore, there is an operation which prevents decline in a dielectric constant and electric insulating degradation by setting particle size to 0.4 micrometers - 1.4 micrometers.
[0007]
[Example] Drawing 1 is the sectional view showing the structure of the thin film capacitor in one example of this invention, and a thin film capacitor consists of the dielectric film 5 and the aluminum up electrode 6 which consist of the polycarbonate (it omits Following PC) substrate 1 which is a printed circuit board made of resin, the aluminum lower electrode 2, compound perovskite oxide powder 3, and hardenability resin 4.
[0008] How to manufacture the thin film capacitor of this example is explained. After carrying out cleaning processing of dimension 50mmx50mmx2mm PC board 1, the aluminum film with a thickness of 1 micrometer was formed with vacuum evaporation technique, aluminum was etched by the photoresist method, and the aluminum lower electrode 2 was formed.
[0009] Next, Pb(Mg1 / 3 Nb 2/3) O3 compounded by the complex polymerization method The spin coat of the solvent which made the ultraviolet-rays hardening resin solvent which uses epoxy acrylate as a principal component distribute compound (PMN) perovskite oxide powder was carried out on PC board 1, and resin hardening by desiccation processing and an ultraviolet radiation exposure of a volatile solvent was performed. The dielectric film 5 which carries out etching clearance of the contact part of the aluminum lower electrode 2 by the photoresist method, and consists of compound perovskite oxide powder 3 and hardenability resin 4 was formed.
[0010] The thickness of the formed dielectric film 5 is 5 micrometers, and repeated and produced a spin coat, desiccation, and resin hardening. At the temperature of 80 degrees C, desiccation processing of a volatile solvent is

time amount 30 minutes, and UV irradiation is amount of energy 65 KJ/m2. The deed temperature rise was suppressed at 150 degrees C or less for time amount 1 minute.
[0011] The volume fraction of the hardenability resin 4 after resin hardening produced the 0.1vol% - 10vol% thing depending on the concentration of the ultraviolet-rays hardening resin material in a solvent. On the dielectric film 5, 1 micrometer of aluminum film was formed with vacuum evaporation technique, it fabricated by the photoresist method, and the aluminum up electrode 6 was formed. The effective area of a thin film capacitor was decided by the part with which the aluminum up electrode 6 and the aluminum lower electrode 2 lapped, and was set to 3mmx2mm by this example.
[0012] A capacity consistency is so large that the capacity consistency of the produced thin film capacitor has a small volume fraction depending on the volume fraction of the hardenability resin 4 in a dielectric film 5. They are 70 nF/cm2 so that drawing 10 may show. In order to obtain the above capacity consistency, the volume fraction of hardenability resin 4 needs to be less than [7vol%]. However, when the volume fraction became less than [0.5vol%], the binding operation of the PMN powder of hardenability resin 4 became weak, and exfoliation of a dielectric film 5 and decomposition arose.
[0013] Therefore, as for the volume fraction of the hardenability resin 4 in a dielectric film 5, it is desirable that it is 0.5vol(s)% - 7vol%. The particle size of PMN powder also influenced the mechanical strength and dielectric characteristics of a dielectric film 5. Since powdered surface area would increase if particle size is set to 0.4 micrometers or less, by the hardenability resin 4 which is 7vol%, the binding operation was weak, the crack arose in the dielectric film 5 and the short circuit was caused electrically. On the other hand, when the particle size of PMN was set to 1.4 micrometers or more, the irregularity of a dielectric film 5 became large and dielectric breakdown voltage deteriorated remarkably. Therefore, as for the particle size of the compound perovskite oxide powder 3, it is desirable that it is 0.4 micrometers - 1.4 micrometers.
[0014] As a compound perovskite oxide, they are TiO(Ba0.7 Sr0.3) 3 (BST), Ba(Mg1 / 3 Ta 2/3) O3 (BMT), and BaTiO3 besides PMN (PLZT (Zr(Pb0.9 La0.1)0.65Ti0.35)). (BT) and SrTiO3 Similarly (ST) was compounded by the complex polymerization method.
[0015] The synthetic approach of PLZT powder is explained as an example. First, titanium tetra-isopropoxide (Ti4 (C3 H7 O)) was dissolved in ethylene glycol / citric-acid solution, and then a zirconium nitrate (Zr(NO3) 2 and H2 O), lead acetate (Pb(CH3 COO)2 and 3H2 O), and an acetic-acid lanthanum (La(CH3 COO)3 and 1.5H2 O) were dissolved. Heating concentration of this solution was carried out, the polyesterification reaction was advanced, and polymer gel was produced. After grinding in a mortar the black powder which was made to decompose this thermally at 350 more degrees C, and was obtained, the powder of light yellow was produced by heat-treating in 2-hour air at 900 degrees C. By powder method X-ray diffraction analysis, it checked that the obtained powder was a perovskite monolayer.
[0016] The result of having investigated the temperature characteristic of the capacity of the thin film capacitor using the above-mentioned compound perovskite oxide powder produced at hardenability resin 5vol% to drawing 11 is shown. Each of PMN25, PLZT24, and BMT23 which are a compound perovskite oxide is 70 nF/cm2. The above capacity value was shown. PMN22 of a temperature change with the largest capacity value is [the temperature characteristic] the largest, and the rate of change in 25 to 125 degrees C is 3500 ppm/degree C. Considering that the rate of change of a PMN ceramic condenser is several %/degree C, this value is very small. BT25 and ST26 which are simple perovskite are 70 nF/cm2. Although it was the following capacity consistencies, the capacity rate of change showed the temperature characteristic respectively good in degree C and 200 ppm /or less.
[0017] The description of this example is to have enabled shaping of what was being fabricated in the conventional ceramic sintering method at the temperature of about 1000 times at 150 degrees C, when a dielectric constant fabricates 3000 to 10,000 or more compound perovskite oxide powder 3 using hardenability resin 4. Moreover, by optimizing powder particle size and the addition of hardenability resin 4, the dielectric film 5 which has high capacity and sufficient reinforcement is offered. Although the value of the effective dielectric constant of a dielectric film 5 serves as one half extent of bulk since the dielectric constant of the hardenability resin 4 which binds the compound perovskite oxide powder 3 is as small as 2-4, the temperature characteristic improves with 1 / 10 - 1/100 of bulk substantially.
[0018] By using the above-mentioned thin film capacitor for printed circuit boards, the thin film CR circuit element of high degree of accuracy and high-reliability can be offered. This sectional view and drawing 4 of the top view of a thin film CR circuit element [in / in drawing 2 / one example of this invention] and drawing 3 are these circuit diagrams. A thin film CR circuit element is formed the epoxy resin layer 8 for carrying out flattening of the irregularity of the front face of PC board 7 and PC board 7, and on it, and is constituted by the thin film capacitor 40 which consists of the resistance element 9 which consisted of Nichrome alloy film, a PMN dielectric film 10, an up electrode 11, and a lower electrode 30.
[0019] One terminal of a resistance element 9 is connected to an input/output terminal 12, and another terminal is joined to the lower electrode 30 and input/output terminal 13 of a thin film capacitor 40. Moreover, the up electrode 11 of a thin film capacitor 40 is connected to the input/output terminal 14. In addition, the up electrode 11 and input/output terminals 12, 13, and 14 have structure which is two-layer structure, respectively, for example, carried out the laminating of the gold films 11b, 12b, 13b, and 14b to order from the substrate side, respectively on the nickel film 11a, 12a, and 13a and 14a.
[0020] moreover — the time of preparing a wrap protective coat for each component or wiring on a substrate, in order to protect each component, and preparing a protective coat — the up electrode 11 and input/output

terminals 12, 13, and 14 — it is desirable to make each part express.
[0021] thus, 1 set of resistance elements 9 and the input/output terminal from a thin film capacitor 40 — three pieces — coming out — **** — two of pieces [them] — it can take and one resistance element as a resistance element, one thin film capacitor or one resistance element, and the serial component of one thin film capacitor can be chosen in the direction. Furthermore, by allotting the resistance element 9 of two or more groups, and CR component of a thin film capacitor 40, CR circuit element of arbitration is producible. 1 chip 6mmx5mm CR circuit element which the effective area of a thin film capacitor 40 becomes from 1.0mmx1.5mm, four thin film capacitors, and four resistance elements was produced.
[0022] The production approach is explained according to drawing 5 - drawing 9 . The spin coat of the epoxy resin was first carried out to the front face of 50mmx50mm PC board 7, it dried at 150 degrees C, and the epoxy resin layer 8 with a thickness of 1 micrometer was formed (drawing 5). This is for making surface irregularity of PC board 7 small, and improving the precision of the dielectric breakdown voltage of a dielectric film, and the resistance of the resistance film, and carried out flattening of the average of roughness height on the front face of a substrate to 0.2 micrometers or less after forming an epoxy resin layer from 0.8 micrometers of the first stage.
[0023] The presentation formed 0.01 micrometers of Nichrome alloy film of nickel/Cr=80/20 with the vacuum deposition method, and the thin line section with a line breadth of 100 micrometers, an input/output terminal 12, the pad section for 13, and the lower electrode 30 section of a thin film capacitor 40 were formed using the photoresist method etc. (drawing 6).
[0024] Production of the PMN dielectric film 10 was performed like the above-mentioned producing method. That is, after applying on a substrate the solvent which made the ultraviolet-rays hardening resin solvent which uses epoxy acrylate as a principal component distribute the PMN powder compounded by the complex polymerization method by the technique of a spin coat etc., resin hardening by desiccation processing and an ultraviolet radiation exposure of a volatile solvent was performed, and etching clearance of the garbage was carried out by the photoresist method (drawing 7).
[0025] The thickness of the formed PMN dielectric film 10 is 5 micrometers, and repeated and produced a spin coat, desiccation, and resin hardening. At the temperature of 80 degrees C, desiccation processing of a volatile solvent is time amount 30 minutes, and UV irradiation is amount of energy 65 KJ/m2. The deed temperature rise was suppressed at 150 degrees C or less for time amount 1 minute. The volume fraction of the hardenability resin after resin hardening was 6vol(s)%.
[0026] Next, while carrying out vacuum deposition of the nickel film 11a, 12a, 13a, and 14a and the gold films 11b, 12b, 13b, and 14b one by one, it was processed by the photoresist method, and input/output terminals 12 and 13 and the up electrode 11 were formed. Gold was formed in the front face for improving the wettability of soldering (drawing 8). The overcoat of the epoxy resin was carried out to the last, and **** opium poppy ******** 21 was formed for the input/output terminal part (drawing 9).
[0027] Thus, as for the capacity of one created capacitor, the 0.010-0.012, and **200 ppm degree C of property of temperature characteristics was acquired 2.7nF**7%, as for dielectric loss tandelta. The resistance of the resistance element of one piece was **25 ppm/degree C in temperature coefficient 10kohm**1%. Since the capacitor element and the resistance element are produced in the thin film process in this invention, the precision of capacity value and resistance is high 10% compared with the conventional chip. Furthermore, generating of the electrical noise by the poor electrical installation between the components which had become a problem conventionally about the component since it was integrating, small and was solvable.
[0028]
[Effect of the Invention] The dielectric film with which a dielectric constant consists of 10,000 or more compound perovskite oxides according to this invention so that clearly from the above example can be produced at the temperature of 150 degrees C or less, and they are 70 nF/cm2 on a printed circuit board. The thin film capacitor of the above capacity consistency can be offered. Furthermore, the RC circuit component using this thin film capacitor has a high precision of capacity value and resistance 10% or more compared with the conventional chip circuit, and can solve the problem of the electrical noise generated by poor soldering. Moreover, although this invention was characterized by low-temperature formation of a dielectric film and the circuit element using a print resin substrate was offered, it is clear this invention's to have effectiveness also about the component for silicon semiconductor integrated circuits and a GaAs compound semiconductor integrated circuit device.

[Translation done.]

TECHNICAL FIELD

[Industrial Application] This invention relates to the thin film capacitor widely used for a public welfare device etc., and its manufacture approach.

[Translation done.]

* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] When forming a thin film capacitor on the printed circuit board made of resin, the cure against heat at the time of the dielectric membrane formation process of having taken into consideration the heat-resistant temperature of a resin substrate is an important technical technical problem. As a conventional technique, it is SiO2 by electron cyclotron resonance vapor growth (ECR-CVD method). The approach of forming the thin film capacitor using the film on a glass epoxy group plate with a heat-resistant temperature of 200 degrees C is announced by the 126th page from the 123rd page (1993) of the 5th microelectronics symposium collected works.

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EFFECT OF THE INVENTION

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TECHNICAL PROBLEM

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[0004] This invention solves said conventional technical problem, and is 70 nF/cm2. While aiming at offering the thin film capacitor which has the above capacity consistency and was excellent in insulation, and its manufacture approach, it aims at offering CR circuit element of high degree of accuracy and high-reliability using it.

[Translation done.]

MEANS

[Means for Solving the Problem] In order to attain this object, particle size fabricated the compound perovskite oxide powder which is 0.4 micrometers - 1.4 micrometers using 0.5vol(s)% - 7vol% hardenability resin as a dielectric film.

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OPERATION

[Function] The dielectric film which uses as a principal component the compound perovskite oxide with which a dielectric constant has thousands or more and is used for a ceramic condenser by the aforementioned means can be formed at the low temperature of 150 degrees C. Hardenability resin is used in order to bind compound perovskite oxide powder, but since the effective dielectric constant of a dielectric film will fall if the volume fraction of hardenability resin increases, 0.5vol% - 7vol% is the optimal. The particle size of compound perovskite oxide acts on a binding property and electric insulation. In 0.4 micrometers or less, surface area becomes large, and it becomes impossible for particle size to fully bind by 7vol% hardenability resin. Moreover, the opening between the grains with which particle size is set to 1.4 micrometers or more becomes large, and electric insulation deteriorates. Therefore, there is an operation which prevents decline in a dielectric constant and electric insulating degradation by setting particle size to 0.4 micrometers - 1.4 micrometers.

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EXAMPLE

[Example] Drawing 1 is the sectional view showing the structure of the thin film capacitor in one example of this invention, and a thin film capacitor consists of the dielectric film 5 and the aluminum up electrode 6 which consist of the polycarbonate (it omits Following PC) substrate 1 which is a printed circuit board made of resin, the aluminum lower electrode 2, compound perovskite oxide powder 3, and hardenability resin 4.
[0008] How to manufacture the thin film capacitor of this example is explained. After carrying out cleaning processing of dimension 50mmx50mmx2mm PC board 1, the aluminum film with a thickness of 1 micrometer was formed with vacuum evaporation technique, aluminum was etched by the photoresist method, and the aluminum lower electrode 2 was formed.
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[0013] Therefore, as for the volume fraction of the hardenability resin 4 in a dielectric film 5, it is desirable that it is 0.5vol(s)% - 7vol%. The particle size of PMN powder also influenced the mechanical strength and dielectric characteristics of a dielectric film 5. Since powdered surface area would increase if particle size is set to 0.4 micrometers or less, by the hardenability resin 4 which is 7vol%, the binding operation was weak, the crack arose in the dielectric film 5 and the short circuit was caused electrically. On the other hand, when the particle size of PMN was set to 1.4 micrometers or more, the irregularity of a dielectric film 5 became large and dielectric breakdown voltage deteriorated remarkably. Therefore, as for the particle size of the compound perovskite oxide powder 3, it is desirable that it is 0.4 micrometers - 1.4 micrometers.
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[0024] Production of the PMN dielectric film 10 was performed like the above-mentioned producing method. That is, after applying on a substrate the solvent which made the ultraviolet-rays hardening resin solvent which uses epoxy acrylate as a principal component distribute the PMN powder compounded by the complex polymerization method by the technique of a spin coat etc., resin hardening by desiccation processing and an ultraviolet radiation exposure of a volatile solvent was performed, and etching clearance of the garbage was carried out by the photoresist method (drawing 7).
[0025] The thickness of the formed PMN dielectric film 10 is 5 micrometers, and repeated and produced a spin coat, desiccation, and resin hardening. At the temperature of 80 degrees C, desiccation processing of a volatile solvent is time amount 30 minutes, and UV irradiation is amount of energy 65 KJ/m2. The deed temperature rise was suppressed at 150 degrees C or less for time amount 1 minute. The volume fraction of the hardenability resin after resin hardening was 6vol(s)%.
[0026] Next, while carrying out vacuum deposition of the nickel film 11a, 12a, 13a, and 14a and the gold films 11b, 12b, 13b, and 14b one by one, it was processed by the photoresist method, and input/output terminals 12 and 13 and the up electrode 11 were formed. Gold was formed in the front face for improving the wettability of soldering (drawing 8). The overcoat of the epoxy resin was carried out to the last, and **** opium poppy ******** 21 was formed for the input/output terminal part (drawing 9).
[0027] Thus, as for the capacity of one created capacitor, the 0.010-0.012, and **200 ppm degree C of property of temperature characteristics was acquired 2.7nF**7%, as for dielectric loss tandelta. The resistance of the resistance

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element of one piece was **25 ppm/degree C in temperature coefficient 10kohm**1%. Since the capacitor element and the resistance element are produced in the thin film process in this invention, the precision of capacity value and resistance is high 10% compared with the conventional chip. Furthermore, generating of the electrical noise by the poor electrical installation between the components which had become a problem conventionally about the component since it was integrating, small and was solvable.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The sectional view showing the structure of the thin film capacitor in one example of this invention
[Drawing 2] The top view of CR circuit element in one example of this invention
[Drawing 3] The sectional view of CR circuit element in one example of this invention
[Drawing 4] The circuit diagram of CR circuit element in one example of this invention
[Drawing 5] Drawing showing the manufacture approach of CR circuit element in one example of this invention
[Drawing 6] Drawing showing the manufacture approach of CR circuit element in one example of this invention
[Drawing 7] Drawing showing the manufacture approach of CR circuit element in one example of this invention
[Drawing 8] Drawing showing the manufacture approach of CR circuit element in one example of this invention
[Drawing 9] Drawing showing the manufacture approach of CR circuit element in one example of this invention
[Drawing 10] Drawing showing the relation between the capacity consistency of a thin film capacitor, and the volume fraction of hardenability resin
[Drawing 11] Drawing showing the temperature characteristic of a thin film capacitor
[Description of Notations]
1 Seven PC board
2 Aluminum Lower Electrode
3 Compound Perovskite Oxide Powder
4 Hardenability Resin
5 Dielectric Film
6 Aluminum Up Electrode
8 Epoxy Resin Layer
9 Resistance Element
10 PMN Dielectric Film
11 Up Electrode
12, 13, 14 Input/output terminal

[Translation done.]

* NOTICES *

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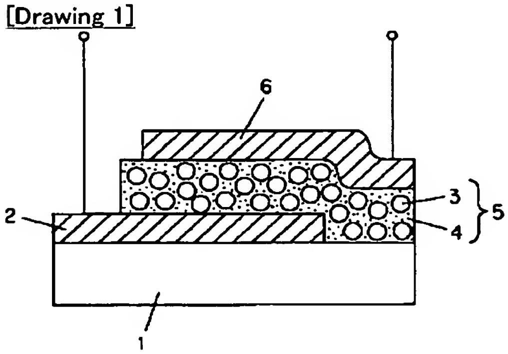
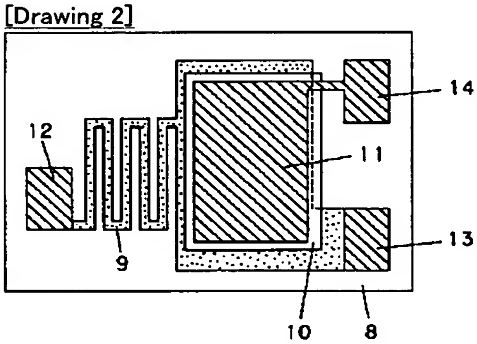
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

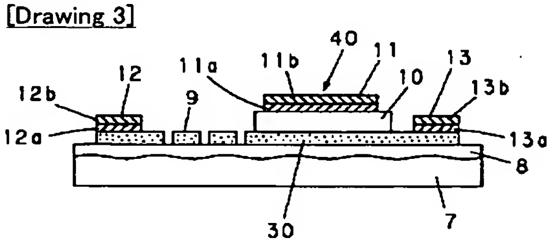
[Drawing 1]



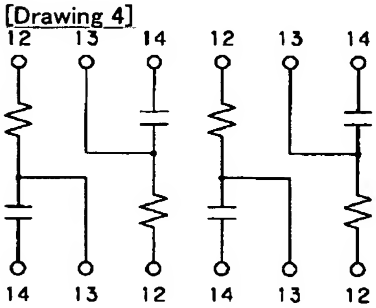
[Drawing 2]



[Drawing 3]



[Drawing 4]



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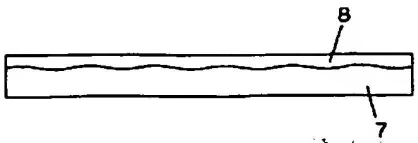
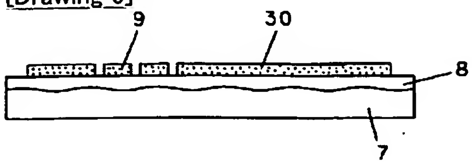
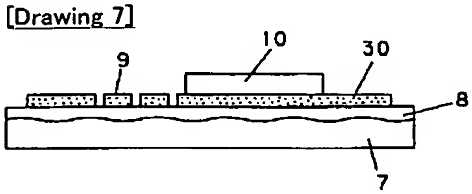


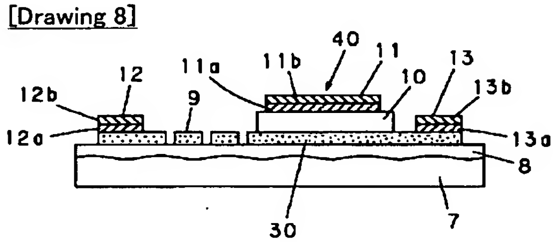
[Drawing 6]



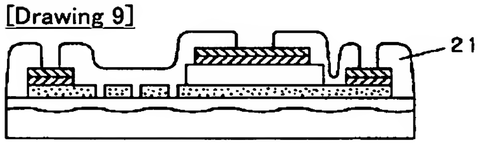
[Drawing 7]



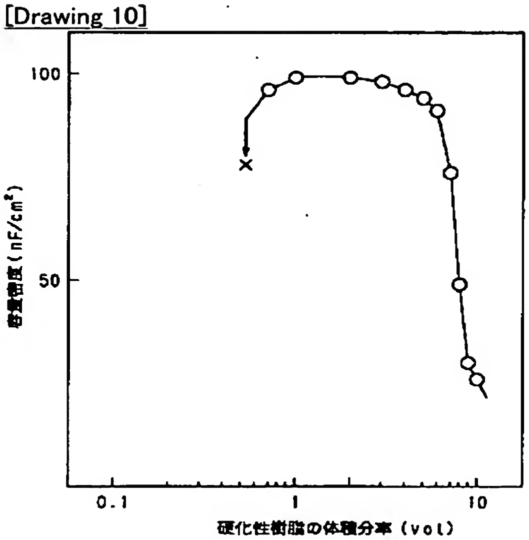
[Drawing 8]



[Drawing 9]



[Drawing 10]



[Drawing 11]

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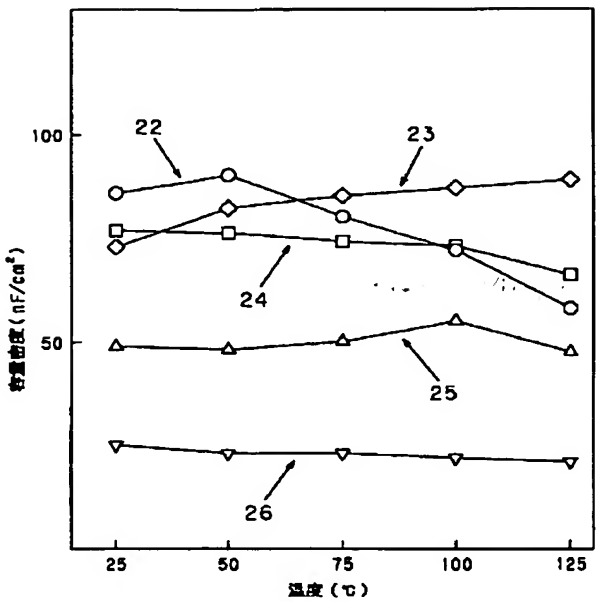

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(19)日本国特許庁（ＪＰ）　(12) 公開特許公報（A）　(11)特許出願公開番号

特開平7－226334

(43)公開日　平成７年(1995) ８月22日

(51)Int.Cl.⁶	識別記号	庁内整理番号	FI		技術表示箇所
Ｈ０１Ｇ　4/33					
4/40					
		9174－5E	Ｈ０１Ｇ　4/ 06	１０２	
		9174－5E	4/ 40	３０７	

審査請求　未請求　請求項の数８　ＯＬ　（全 ６ 頁）

(21)出願番号　特願平6－15180

(22)出願日　平成６年(1994) ２月９日

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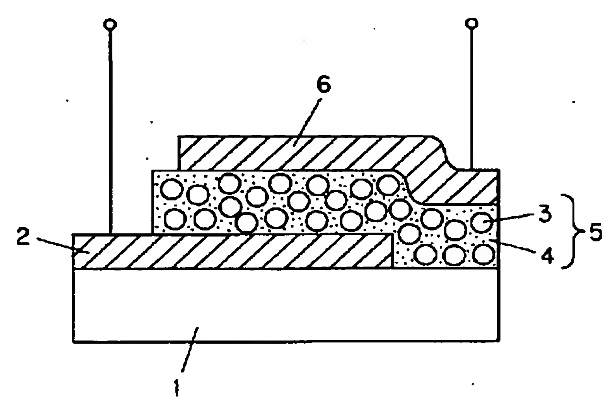
(54)【発明の名称】　薄膜コンデンサ及びその製造方法

(57)【要約】

【目的】　１５０℃以下の温度で作製でき、７０ｎＦ／ｃｍ² 以上の容量密度を有し、かつ、絶縁性に優れた薄膜コンデンサ及びその製造方法とともに、それを用いた高精度・高信頼性のＣＲ回路素子を提供することを目的としている。

【構成】　薄膜コンデンサは樹脂製プリント基板であるＰＣ（ポリカーボネイト）基板１、アルミ下部電極２、複合ペロブスカイト酸化物粉末３と硬化性樹脂４から構成される誘電体膜５、及びアルミ上部電極６からなる。誘電率が数千以上の複合ペロブスカイト酸化物粉末３を硬化性樹脂４を含有する揮発性溶媒に分散させてスピンコート法でＰＣ基板３上に塗布した後、８０℃で揮発溶媒の乾燥除去、紫外光照射によって樹脂硬化することにより、１５０℃以下で誘電体膜５を形成する。



【特許請求の範囲】

【請求項１】下部電極と上部電極との間に誘電体膜を設けた薄膜コンデンサであって、誘電体膜として複合ペロブスカイト酸化物と硬化性樹脂の混合体を用いたことを特徴する薄膜コンデンサ。

【請求項２】複合ペロブスカイト酸化物を粉末とし、その粉末の粒径が０．４μｍ～１．４μｍであることを特徴とする請求項１記載の薄膜コンデンサ。

【請求項３】複合ペロブスカイト酸化物を粉末とし、その粉末への硬化性樹脂の添加量が０．５ｖｏｌ％～７ｖｏｌ％であることを特徴とする請求項１記載の薄膜コンデンサ。

【請求項４】硬化性樹脂として紫外線硬化樹脂を用いたことを特徴とする請求項１記載の薄膜コンデンサ。

【請求項５】複合ペロブスカイト酸化物の主成分が、組成式がABO_3で表されＡとしてＰｂ，Ｓｒ，Ｂａ，Ｌａの少なくとも１種を含有し、ＢとしてＴｉ，Ｚｒ，Ｔａ，Ｍｇ，Ｎｂの少なくとも１種を含有することを特徴とする請求項１記載の薄膜コンデンサ。

【請求項６】基板上に下部電極を形成し、前記下部電極上に複合ペロブスカイト酸化物粉末と硬化性樹脂の混合体を設けてその後に１５０℃以下の温度で前記硬化樹脂を硬化させて誘電体膜を形成し、前記誘電体膜の上に上部電極を形成したことを特徴とする薄膜コンデンサの製造方法。

【請求項７】硬化性樹脂を紫外線硬化樹脂とし、紫外線を照射して誘電体膜を形成することを特徴とする請求項６記載の薄膜コンデンサの製造方法。

【請求項８】抵抗とコンデンサを電気的に結合したＣＲ回路素子であって、コンデンサとして請求項１記載の薄膜コンデンサを用いたことを特徴とするＣＲ回路素子。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は民生機器等に広く用いられる薄膜コンデンサ及びその製造方法に関するものである。

【０００２】

【従来の技術】樹脂製プリント基板上に薄膜コンデンサを形成する場合、樹脂基板の耐熱温度を考慮した誘電体成膜プロセス時の熱対策は重要な技術課題である。従来技術としては、電子サイクロトロン共鳴気相成長法（ＥＣＲ－ＣＶＤ法）によってSiO_2膜を用いた薄膜コンデンサを耐熱温度２００℃のガラスエポキシ基板上に形成する方法が、第５回マイクロエレクトロニクスシンポジウム論文集（１９９３年）第１２３ページから第１２６ページに発表されている。

【０００３】

【発明が解決しようとする課題】ＥＣＲ－ＣＶＤ法で形成されたSiO_2誘電体膜コンデンサの容量密度は１３．１ｎＦ／cm^2と実用レベルの特性が得られているが、コストパフォーマンスを考えると５倍以上の容量密度が要求される。５倍の容量密度を達成するためには誘電体膜厚を１／５の６０ｎｍにしなければならず、絶縁性が劣化する問題があった。

【０００４】本発明は前記従来の課題を解決するもので、７０ｎＦ／cm^2以上の容量密度を有し、かつ、絶縁性に優れた薄膜コンデンサ及びその製造方法を提供することを目的とするとともに、それを用いた高精度・高信頼性のＣＲ回路素子を提供することを目的としている。

【０００５】

【課題を解決するための手段】この目的を達成するために、誘電体膜として粒径が０．４μｍ～１．４μｍの複合ペロブスカイト酸化物粉末を０．５ｖｏｌ％～７ｖｏｌ％の硬化性樹脂を用いて成形した。

【０００６】

【作用】前記の手段により、誘電率が数千以上を有しセラミックコンデンサに用いられる複合ペロブスカイト酸化物を主成分とする誘電体膜を１５０℃の低温度で形成することができる。硬化性樹脂は複合ペロブスカイト酸化物粉末をバインディングするために用いられるが、硬化性樹脂の体積分率が多くなると誘電体膜の実効誘電率が低下してしまうので、０．５ｖｏｌ％～７ｖｏｌ％が最適である。複合ペロブスカイト酸化物の粒径はバインディング特性と電気的絶縁性に作用する。粒径が０．４μｍ以下では表面積が大きくなり、７ｖｏｌ％の硬化性樹脂では十分にバインディングできなくなる。また、粒径が１．４μｍ以上になると粒間の空隙が大きくなり電気的絶縁性が劣化する。従って、粒径を０．４μｍ～１．４μｍとすることによって誘電率の低下と電気的絶縁性の劣化を防ぐ作用がある。

【０００７】

【実施例】図１は本発明の一実施例における薄膜コンデンサの構造を示す断面図で、薄膜コンデンサは樹脂製プリント基板であるポリカーボネイト（以下ＰＣと略す）基板１、アルミ下部電極２、複合ペロブスカイト酸化物粉末３と硬化性樹脂４からなる誘電体膜５、アルミ上部電極６からなる。

【０００８】本実施例の薄膜コンデンサを製造する方法について説明する。寸法５０ｍｍ×５０ｍｍ×２ｍｍのＰＣ基板１を脱脂処理した後、厚さ１μｍのアルミ膜を真空蒸着法で成膜し、フォトレジスト法でアルミをエッチングしてアルミ下部電極２を形成した。

【０００９】次に錯体重合法で合成した$Pb(Mg_{1/3}Nb_{2/3})O_3$（ＰＭＮ）複合ペロブスカイト酸化物粉末をエポキシアクリレートを主成分とする紫外線硬化樹脂溶媒に分散させた溶剤をＰＣ基板１上にスピンコートし、揮発性溶媒の乾燥処理と紫外光照射による樹脂硬化を行った。フォトレジスト法でアルミ下部電極２のコンタクト部分をエッチング除去して複合ペロブスカイト酸

化物粉末３と硬化性樹脂４からなる誘電体膜５を形成した。

【００１０】その形成した誘電体膜５の膜厚は５μmで、スピンコート、乾燥、樹脂硬化を繰り返して作製した。揮発性溶媒の乾燥処理は温度８０℃で時間３０分、紫外線照射はエネルギー量６５ＫＪ／m^2 で時間１分行い温度上昇は１５０℃以下に抑えた。

【００１１】樹脂硬化後の硬化性樹脂４の体積分率は溶剤中の紫外線硬化樹脂材の濃度に依存し、０．１ｖｏｌ％～１０ｖｏｌ％のものを作製した。誘電体膜５上にアルミ膜を真空蒸着法で１μm成膜し、フォトレジスト法で成形してアルミ上部電極６を形成した。薄膜コンデンサの実効面積はアルミ上部電極６とアルミ下部電極２が重なった部分で決まり、本実施例では３ｍｍ×２ｍｍとした。

【００１２】作製した薄膜コンデンサの容量密度は誘電体膜５中の硬化性樹脂４の体積分率に依存し、体積分率が小さいほど容量密度は大きい。図１０からわかるように７０ｎＦ／ｃm^2 以上の容量密度を得るためには硬化性樹脂４の体積分率は７ｖｏｌ％以下であることが必要である。しかし、体積分率が０．５ｖｏｌ％以下になると硬化性樹脂４のPMN粉末のバインディング作用が弱くなり、誘電体膜５の剥離、分解が生じた。

【００１３】従って、誘電体膜５中の硬化性樹脂４の体積分率は０．５ｖｏｌ％～７ｖｏｌ％であることが望ましい。PMN粉末の粒径も誘電体膜５の機械的強度と誘電特性に影響した。粒径が０．４μm以下になると粉末の表面積が増大するため７ｖｏｌ％の硬化性樹脂４ではバインディング作用が弱く、誘電体膜５にクラックが生じて電気的に短絡を起こした。一方、PMNの粒径が１．４μm以上になると誘電体膜５の凹凸が大きくなり絶縁破壊電圧が著しく劣化した。従って、複合ペロブスカイト酸化物粉末３の粒径は０．４μm～１．４μmであることが望ましい。

【００１４】複合ペロブスカイト酸化物としてはPMNの他に（$Pb_{0.9}La_{0.1}$）（$Zr_{0.65}Ti_{0.35}$）（PLZT）、（$Ba_{0.7}Sr_{0.3}$）TiO_3（BST）、$Ba(Mg_{1/3}Ta_{2/3})O_3$（BMT）、$BaTiO_3$（BT）、$SrTiO_3$（ST）を同じく錯体重合法によって合成した。

【００１５】例として、ＰＬＺＴ粉末の合成方法を説明する。先ず、チタニウムテトライソプロポキシド（$Ti(C_3H_7O)_4$）をエチレングリコール／クエン酸溶液に溶解させ、次に硝酸ジルコニウム（$Zr(NO_3)_2\cdot H_2O$）、酢酸鉛（$Pb(CH_3COO)_2\cdot 3H_2O$）、酢酸ランタン（$La(CH_3COO)_3\cdot 1.5H_2O$）を溶解させた。この溶液を加熱濃縮し、ポリエステル化反応を進行させて高分子ゲルを作製した。これをさらに３５０℃で加熱分解させて得られた黒色の粉末を乳鉢中で粉砕した後、９００℃で２時間空気中で熱処理することにより淡黄色の粉末を作製した。粉末法Ｘ線回折分析により、得られた粉末がペロブスカイト単層であることを確認した。

【００１６】図１１に硬化性樹脂５ｖｏｌ％で作製した上記の複合ペロブスカイト酸化物粉末を用いた薄膜コンデンサの容量の温度特性を調べた結果を示す。複合ペロブスカイト酸化物であるPMN２５，ＰＬＺＴ２４，ＢＭＴ２３はいずれも７０ｎＦ／ｃm^2 以上の容量値を示した。温度特性は容量値が一番大きいPMN２２が最も温度変化が大きく、２５℃から１２５℃での変化率は３５００ｐｐｍ／℃である。この値はPMNセラミックコンデンサの変化率が数％／℃であることを考えると極めて小さい。単純ペロブスカイトであるＢＴ２５，ＳＴ２６は７０ｎＦ／ｃm^2 以下の容量密度であるが、その容量変化率はそれぞれ２００ｐｐｍ／℃以下と良好な温度特性を示した。

【００１７】本実施例の特徴は誘電率が３千から１万以上の複合ペロブスカイト酸化物粉末３を硬化性樹脂４を用いて成形することにより、従来のセラミック焼結法では千度近い温度で成形していたものを、１５０℃で成形可能にしたことにある。また粉末粒径と硬化性樹脂４の添加量を最適化することによって、高容量かつ十分な強度を有する誘電体膜５を提供するものである。複合ペロブスカイト酸化物粉末３をバインディングする硬化性樹脂４の誘電率は２～４と小さいので誘電体膜５の実効誘電率の値はバルクの半分程度となるが、温度特性はバルクの１／１０～１／１００と大幅に改善される。

【００１８】上記プリント基板用薄膜コンデンサを用いることで、高精度かつ高信頼性の薄膜ＣＲ回路素子を提供することができる。図２は本発明の一実施例における薄膜ＣＲ回路素子の平面図、図３は同断面図、図４は同回路図である。薄膜ＣＲ回路素子はＰＣ基板７、ＰＣ基板７の表面の凹凸を平坦化するためのエポキシ樹脂層８、その上に形成され、ニクロム合金膜で構成された抵抗素子９、PMN誘電体膜１０，上部電極１１，下部電極３０より構成される薄膜コンデンサ４０によって構成される。

【００１９】抵抗素子９の一方の端子は入出力端子１２へ接続され、もう一方の端子は薄膜コンデンサ４０の下部電極３０及び入出力端子１３に接合される。また薄膜コンデンサ４０の上部電極１１は入出力端子１４へ接続されている。なお、上部電極１１及び入出力端子１２，１３，１４はそれぞれ２層構造となっており、例えば基板側からニッケル膜１１ａ，１２ａ，１３ａ，１４ａ上にそれぞれ金膜１１ｂ，１２ｂ，１３ｂ，１４ｂを順に積層した構造となっている。

【００２０】また各素子を保護するために各素子や配線を覆う保護膜を基板上に設けてもよく、保護膜を設ける際には、上部電極１１及び入出力端子１２，１３，１４それぞれの一部を表出させることが好ましい。

【００２１】このように１組の抵抗素子９と薄膜コンデンサ４０からは入出力端子が３個でており、そのうちの２個の取り方で抵抗素子としての抵抗素子１個、薄膜コンデンサ１個、あるいは抵抗素子１個と薄膜コンデンサ１個の直列素子を選ぶことができる。更に複数の組の抵抗素子９と薄膜コンデンサ４０のＣＲ素子を配することにより、任意のＣＲ回路素子を作製することができる。薄膜コンデンサ４０の実効面積が１．０mm×１．５mm、薄膜コンデンサ４個、抵抗素子４個からなる１チップ６mm×５mmのＣＲ回路素子を作製した。

【００２２】図５～図９に従って作製方法を説明する。先ず５０mm×５０mmのＰＣ基板７の表面にエポキシ樹脂をスピンコートして１５０℃で乾燥し、厚さ１μmのエポキシ樹脂層８を形成した（図５）。これはＰＣ基板７の表面凹凸を小さくして誘電体膜の絶縁破壊電圧と抵抗膜の抵抗値の精度を改善するためであり、基板表面の平均粗さを初期の０．８μmからエポキシ樹脂層を形成後０．２μm以下へと平坦化した。

【００２３】真空蒸着法で組成がＮｉ／Ｃｒ＝８０／２０のニクロム合金膜を０．０１μm成膜し、フォトレジスト法等を用いて線幅１００μmの細線部、入出力端子１２，１３用のパッド部、薄膜コンデンサ４０の下部電極３０部を形成した（図６）。

【００２４】PMN誘電体膜１０の作製は前述の作製法と同様に行った。即ち、錯体重合法で合成したPMN粉末をエポキシアクリレートを主成分とする紫外線硬化樹脂溶媒に分散させた溶剤をスピンコート等の手法によって基板上に塗布した後に揮発性溶媒の乾燥処理と紫外光照射による樹脂硬化を行い、フォトレジスト法で不要部分をエッチング除去した（図７）。

【００２５】形成したPMN誘電体膜１０の膜厚は５μmで、スピンコート、乾燥、樹脂硬化を繰り返して作製した。揮発性溶媒の乾燥処理は温度８０℃で時間３０分、紫外線照射はエネルギー量６５ＫＪ／m^2 で時間１分行い温度上昇は１５０℃以下に抑えた。樹脂硬化後の硬化性樹脂の体積分率は６ｖｏｌ％であった。

【００２６】次にニッケル膜１１ａ，１２ａ，１３ａ，１４ａと金膜１１ｂ，１２ｂ，１３ｂ，１４ｂを順次真空蒸着するとともにフォトレジスト法により加工して、入出力端子１２，１３及び上部電極１１を形成した。表面に金を形成したのは半田付けの濡れ性をよくするためである（図８）。最後にエポキシ樹脂をオーバーコートし、入出力端子部分を窓開けして保護膜２１を形成した（図９）。

【００２７】このように作成されたコンデンサ１個の容量は２．７ｎＦ±７％、誘電損失ｔａｎδは０．０１０～０．０１２、温度特性±２００ｐｐｍ℃の特性が得られた。抵抗素子は１個の抵抗値が１０ｋΩ±１％、温度係数±２５ｐｐｍ/℃であった。本発明では薄膜プロセスでコンデンサ素子と抵抗素子を作製しているので容量値と抵抗値の精度が従来のチップ部品に比べて１０％高い。更に素子を小型・集積化しているために従来問題になっていた素子間の電気的接続不良による電気的ノイズの発生を解決できた。

【００２８】

【発明の効果】以上の実施例から明らかなように、本発明によれば誘電率が１万以上の複合ペロブスカイト酸化物からなる誘電体膜を１５０℃以下の温度で作製することができ、プリント基板上に７０ｎＦ／cm^2 以上の容量密度の薄膜コンデンサを提供することができる。更にこの薄膜コンデンサを用いたＲＣ回路素子は従来のチップ部品回路に比べて容量値と抵抗値の精度が１０％以上高く、半田付け不良などによって発生していた電気的ノイズの問題を解決することができる。また、本発明は誘電体膜の低温形成を特徴としてプリント樹脂基板を用いた回路素子を提供したが、本発明はシリコン半導体集積回路用素子、ＧａＡｓ化合物半導体集積回路素子についても効果を有することは明らかである。

【図面の簡単な説明】

【図１】本発明の一実施例における薄膜コンデンサの構造を示す断面図

【図２】本発明の一実施例におけるＣＲ回路素子の平面図

【図３】本発明の一実施例におけるＣＲ回路素子の断面図

【図４】本発明の一実施例におけるＣＲ回路素子の回路図

【図５】本発明の一実施例におけるＣＲ回路素子の製造方法を示す図

【図６】本発明の一実施例におけるＣＲ回路素子の製造方法を示す図

【図７】本発明の一実施例におけるＣＲ回路素子の製造方法を示す図

【図８】本発明の一実施例におけるＣＲ回路素子の製造方法を示す図

【図９】本発明の一実施例におけるＣＲ回路素子の製造方法を示す図

【図１０】薄膜コンデンサの容量密度と硬化性樹脂の体積分率との関係を示す図

【図１１】薄膜コンデンサの温度特性を示す図

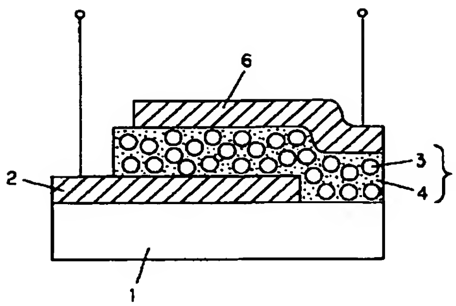
【符号の説明】

１，７　ＰＣ基板
２　アルミ下部電極
３　複合ペロブスカイト酸化物粉末
４　硬化性樹脂
５　誘電体膜
６　アルミ上部電極
８　エポキシ樹脂層
９　抵抗素子
１０　PMN誘電体膜

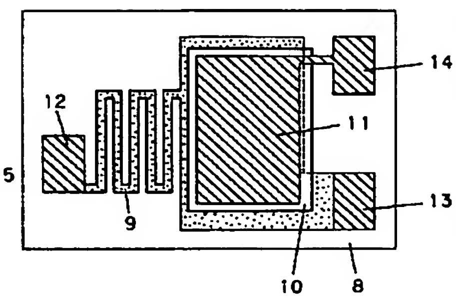
１１　上部電極

１２，１３，１４　入出力端子

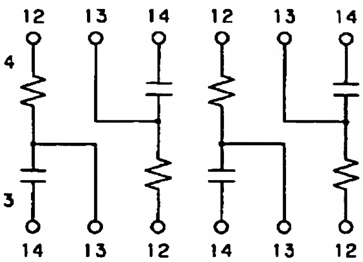
【図１】



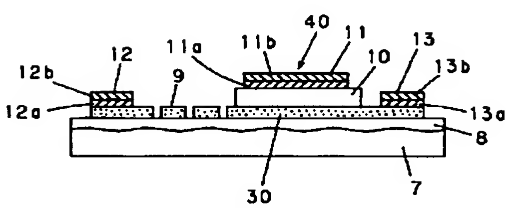
【図２】



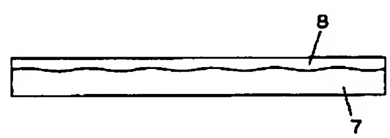
【図４】



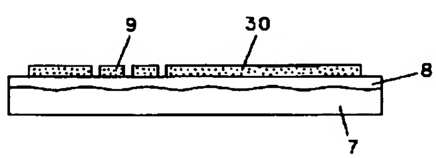
【図３】



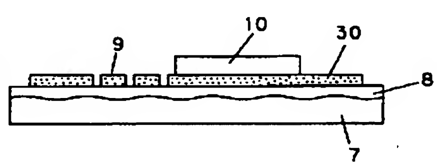
【図５】



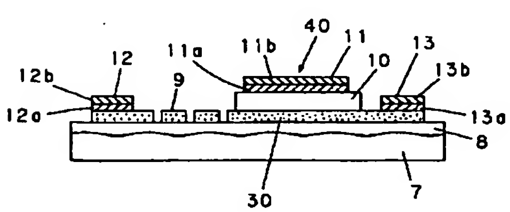
【図６】



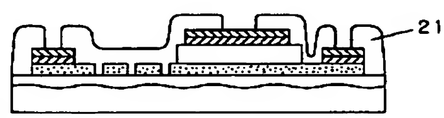
【図７】



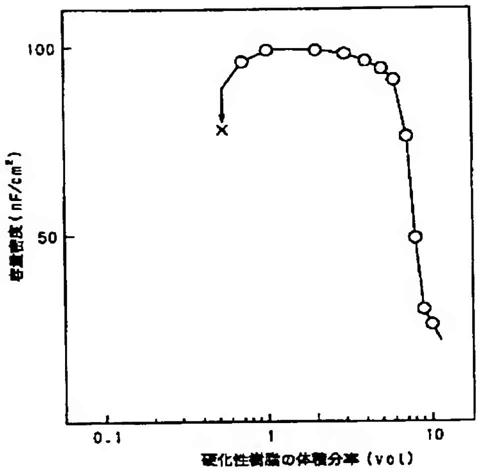
【図８】



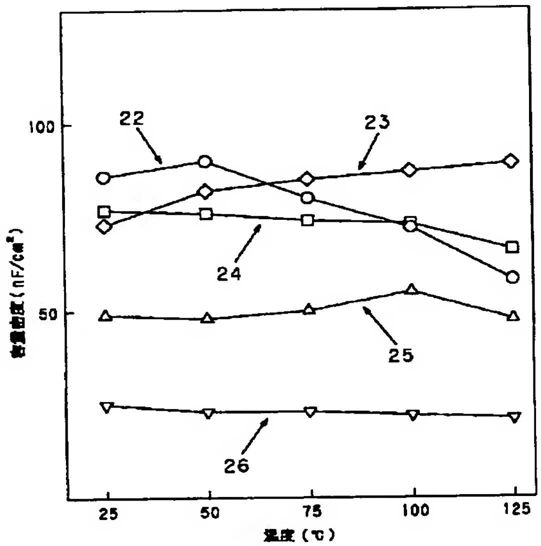
【図９】



【図１０】


100
50
0.1
1
10
容量密度（nF/cm²）
硬化性樹脂の体積分率（vol）

【図１１】


100
50
22
23
24
25
26
25
50
75
100
125
容量密度（nF/cm²）
温度（℃）